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14. ABSTRACT Sulfuric acid particles in the atmosphere are tiny chemical reactors that convert benign gases such as HCl and HBr into Cl ₂ , ClBr, and Br ₂ , which catalytically destroy ozone. These aerosol droplets may also contain organic molecules (emanating from the ocean and land), which may and coat the surface of the aerosol particles. Gas-liquid scattering experiments show that these surfactant coatings can suppress ozone destruction by inhibiting the uptake of HCl into the acid droplets if the organic molecules pack tightly enough at the surface to impede gas transport. Remarkably, the scattering experiments indicate that these organic molecules more often enhance gas uptake because they do not pack tightly but contain functional groups that act as interfacial dissociation sites for HCl and HBr. Short-chain alcohols such as butanol always enhance HCl uptake because HCl and HBr protonate ROH groups, forcing the halide and hydrogen ions into the acid. Pentanoic acid also enhances uptake because HCl can protonate the -COOH group, but butyl and hexyl amine always suppress HCl uptake because the -NH ₂ group is already protonated by the acid. These studies provide a rich picture of the "surface organic chemistry" of sulfuric acid and how it controls the uptake of ozone-destroying gases.					
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Molecular Beams Studies of Gas Transport and Reactions at the Surface of Surfactant-Coated Sulfuric Acid

Gilbert M. Nathanson, Department of Chemistry, University of Wisconsin-Madison

Final Technical Report 02/01/2007 through 11/30/2009

Dr. Michael Berman, Program Director

Objectives and Accomplishments

This technical report summarizes our studies of reactions of the atmospheric gas HCl with bare and surfactant-coated supercooled sulfuric acid at acid concentrations typical of aerosols in the upper troposphere and lower stratosphere. Our investigations over the last three years include investigations of carboxylic acids, amines, and branched alcohols, with the goal of developing a “surface organic chemistry” of sulfuric acid and how it alters reactions that destroy ozone in the atmosphere. We specifically focus on the effect of organic molecules on the uptake of gaseous HCl into 60 and 68 wt % sulfuric acid at -60 °C, which is typical of atmospheric conditions in the upper troposphere and lower stratosphere. This uptake is important because HCl may react with other dissolved species, such as HOCl and ClONO₂, to create gaseous Cl₂, a halogen that catalytically destroys ozone,

Our overall objective since funding began in 1996 has been to develop a microscopic description of collisions and reactions of atmospheric gases with sulfuric acid aerosols that are responsible for altering the levels of ozone, N₂O₅, and halogen-containing gases in the atmosphere. In the last two grant periods, we have extended our gas-liquid scattering studies to explore the even richer chemistry that occurs when aqueous solutions are coated with organic surfactants. This research is motivated by discoveries from aerosol field measurements that aqueous droplets in the upper troposphere contain significant quantities of organic molecules. These molecules typically incorporate functional groups (such as -OH, -COOH, and -NH₂) that make them surface active, creating coatings that may impede gas uptake and alter the rates of chemical reactions that occur near the surface and in the bulk of sulfuric acid droplets. Thus,

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these films may act as barriers to gas uptake that would reduce gas-liquid reactions and suppress ozone depleting processes.

Our studies over the last three years reveal the remarkably diverse behavior of surfactants in controlling gas transport and gas uptake. In most cases, the results are surprising and challenge widely-held views of the nature of surfactants as barriers to gas transport. The experiments show that many short-chain surfactants form porous monolayers at the surface of sulfuric acid. In particular, we have explored the behavior of alcohols (butanol and hexanol), carboxylic acids (pentanoic acid), and amines (butyl and hexylamine). We find that they can impose a barrier (to N_2O_5 hydrolysis), be “invisible” (to water evaporation), or even enhance gas uptake (of HCl). The transition from obstacle to catalyst can be traced to specific interactions between the surfactant and each gas: the hydrolysis of N_2O_5 may be impeded because of its large size and because alcohol molecules that straddle the interface limit contact between N_2O_5 and its H_3O^+ and H_2O reaction partners, while these same alcohol molecules assist HCl dissociation because the alcohol OH groups provide extra interfacial protonation sites. Interestingly, butanol does not impede water evaporation, in part because the butyl chains pack much more loosely than insoluble, long-chain surfactants. Through these investigations, we have gained insight into the mechanisms by which surfactants on sulfuric acid and other aqueous solutions affect transport and reactivity at the gas-liquid interface.

We can summarize our investigations of surfactant-coated sulfuric acid in six statements:

- 1) Short-chain organic molecules spontaneously segregate to the surface of cold sulfuric acid but form porous, poorly packed monolayers that reach less than 2/3 of maximum coverage at -60 °C. These molecules include four carbon chains (butanol, butylamine, and pentanoic acid) and six carbon chains (hexanol, hexylamine, and 2-ethylbutanol). The chains do not pack tightly at 100% coverage even at saturation because of charge repulsion among the protonated ROH head groups, which pushes the chains apart.
- 2) Water evaporation from 56 to 68 wt % sulfuric acid remains unchanged or is reduced only slightly in the presence of these surfactants, most likely because they are so porous. This

result implies that the condensation of water will also be unimpeded by the presence of butanol. We therefore predict that short-chain surfactants will not greatly effect the growth or evaporation of aqueous acid aerosols in the atmosphere.

- 3) The uptake of HCl and HBr into sulfuric acid aerosols is enhanced by up to twofold in the presence of alcohol and carboxylic head groups unless the chains pack tightly enough to impede uptake. On bare sulfuric acid, HCl and HBr most likely enter the acid by protonating H_2O molecules at the surface of the acid and dissolving as H^+ and Cl^- . With alcohol and carboxylic acid surfactants, the extra OH and COOH groups provide extra protonation sites for HCl and HBr. Instead of impeding HCl and HBr transport, the alcohol surfactants therefore “tease” HCl and HBr into the acid. At high surfactant concentrations, the hexanol and pentanoic acid pack tightly enough to slightly impede HCl uptake.
- 4) The hydrolysis of N_2O_5 is impeded by butanol and hexanol films on sulfuric acid, dropping to $\frac{1}{2}$ its value in the presence of hexanol. This observation is in strong contrast to the enhancement in uptake of HCl and HBr by butanol and hexanol. N_2O_5 hydrolysis may be impeded because N_2O_5 is larger than HCl or HBr or because the surfactant chains reduce the availability of H^+ in the interfacial region, a key reactant required for hydrolysis.
- 5) Chain branching (such as in 2-ethylbutanol) actually increases the blocking power of the alcohol rather than diminishes it, in contrast to the expectation the branching would make the surfactant molecules pack less well.
- 6) In contrast to alcohol and carboxylic acid surfactants, butyl and hexylamine only impede the uptake of HCl into sulfuric acid. This resistance arises because the amines are already protonated in sulfuric acid and therefore do not provide extra interfacial dissociation sites for incoming HCl.

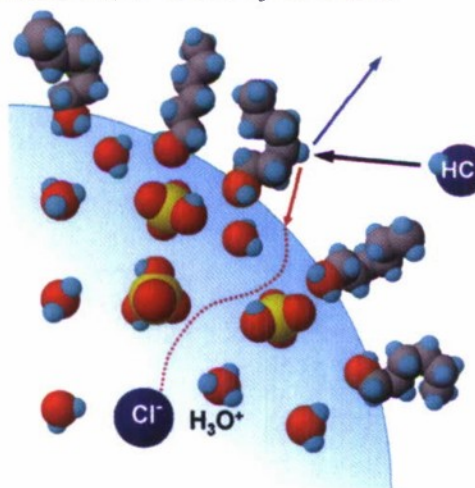
Publications

Our specific accomplishments are outlined below according to their publication. The first two articles were selected as cover art.

“Surfactant Control of Gas Transport and Reactions at the Surface of Sulfuric Acid”,

Seong-Chan Park, Daniel K. Burden, and Gilbert M. Nathanson, *Accounts of Chemical Research*, 42, 379 (2009). Featured on the cover.

This review article summarizes our studies of reactions of HCl, HBr, N_2O_5 , and H_2O with sulfuric acid droplets coated with butanol and hexanol. We directly compare the enhancement of HCl and HBr entry into the acid with the resistance to N_2O_5 uptake (50% reduction for hexanol and 33% reduction for butanol) and postulate that the alcohol molecules

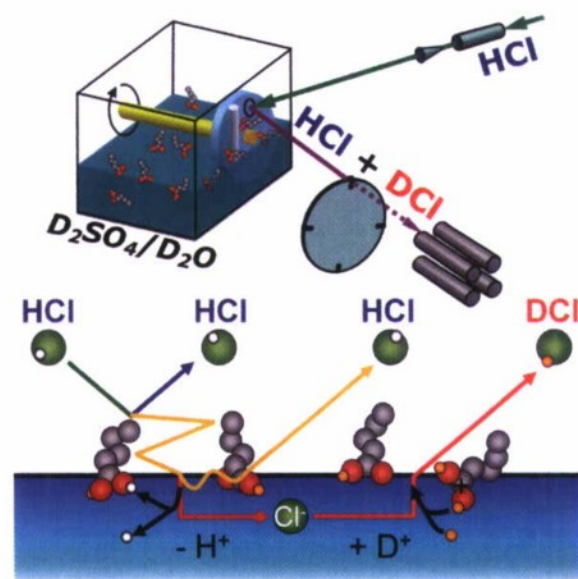


crowd the surface region, reducing the availability of near-interfacial H_3O^+ and H_2O that participate in the conversion of N_2O_5 to HNO_3 . Because this hydrolysis reaction is the most important heterogeneous reaction in the atmosphere in controlling ozone depletion, the ability of surfactants to impede this reaction has potentially enormous implications for ozone levels if surfactants are found in high concentration in upper tropospheric aerosols.

“HCl Uptake through Films of Pentanoic Acid and Pentanoic Acid/Hexanol Mixtures at the Surface of Sulfuric Acid”, Daniel K. Burden, Alexis M. Johnson, and Gilbert M. Nathanson, *Journal of Physical Chemistry A*, 113, 14131 (2009). Featured on cover.

This article combines three separate studies and is our most detailed report yet on surfactant-controlled reactions. Surface tension measurements show that pentanoic acid reaches a coverage of roughly 50% of maximum possible packing, and even the addition of a small amount of the more surface active hexanol molecule pushes it away from the surface. Pentanoic

acid is also not as effective as hexanol in enhancing the entry of HCl because the COOH group is not as basic as the OH group, and is therefore not as good a dissociation site for HCl. We used this data to develop a quantitative model of gas entry through surfactants that involves two steps: transport through the alkyl chains and dissociation at the buried COOH and OH head groups. The two-parameter model works amazingly well in



predicting HCl uptake through hexanol and pentanoic acid films, and provides good evidence that transport between the alkyl chains and dissociation by the head groups can be treated as separate events. They also suggest that gas transport may be described through a “universal” set of blocking and enhancement parameters, such that the butyl chain of pentanoic acid, butanol, and butyl amine may behave roughly similarly for the three surfactants. Even more remarkably, the model can be used to predict the behavior of mixtures of surfactants, potentially making it a powerful tool for predicting actual mixtures.

“The effect of Surfactant Chain Branching on HCl Uptake into Sulfuric Acid”, Daniel K. Burden, Alexis M. Johnson, and Gilbert M. Nathanson, manuscript in preparation

We began this study with a simple expectation: branched surfactant molecules would pack less well at the surface of sulfuric acid and therefore impede HCl uptake less. We chose 2-ethylbutanol as the branched surfactant and compared it with the straight chain analog, 1-hexanol. Our studies show that this expectation is incorrect! The branched surfactant is *more* effective in blocking HCl uptake at the same surfactant concentration. This result appears to be due to better packing of the branched molecule, which can be modeled as a “ball” with a butyl chain. This result is unparalleled in our search through the literature, indicating that short-chain

branched molecules behave very differently from long-chain branched molecules, which always pack less well than their straight-chain analogs.

“Blocking HCl Transport into Supercooled Sulfuric Acid with Alkyl Amines”, Alexis M. Johnson Daniel K. Burden, and Gilbert M. Nathanson, manuscript in preparation

In our final study of surfactants on sulfuric acid, we wanted to understand what would happen when the surfactant molecule contained a functional group more basic than -OH and -COOH . One example are the alkyl amines (-NH_2), which are also important atmospherically. Would they act as better dissociation sites for incoming HCl molecules? In fact, these studies show that the butylamine and hexylamine only block HCl uptake and never enhance it! This is because the amines are so basic that they are immediately protonated by sulfuric acid and therefore converted into RNH_3^+ and so do not present a protonatable nitrogen atom to the incoming HCl molecules. This result also shows that the butyl group is not “invisible” to HCl molecules, as we previously thought, based on the observations that butanol only enhances HCl uptake and never impedes it.

The cumulative studies over the past six years reflect the rich organic chemistry of alcohols, carboxylic acids, and amines sitting at the surface of sulfuric acid, and their ability to block and enhance gas uptake under a wide variety of conditions. We hope that future field measurements in the upper troposphere will be aided by our studies, which provide a framework for predicting the effects of surfactants on ozone depletion and gas-aerosol reactions in the atmosphere.